

# REGENERATION OF SPENT PICKLE LIQUOR

BY B. P. MARTINEZ

\* \* \* \* \* Information Circular 7672



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B. P. Martinez<sup>1/</sup>

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## SUMMARY

A process for regenerating spent pickle liquor is proposed in which some of the water is evaporated at atmospheric pressure and ferrous sulfate is precipitated as monohydrate crystals. Equilibrium conditions are set for a slurry of crystals in a mother liquor containing 5 percent  $\text{FeSO}_4$  and 45 percent  $\text{H}_2\text{SO}_4$ , by weight, and boiling at about  $235^\circ\text{F}$ . The slurry is pumped continuously to a filter, and the mother liquor from the filter is pumped back for reuse in the pickling tanks. The net result of the process is to remove ferrous sulfate in the regeneration plant at the same rate as it is produced in the pickling tanks.

This process is integrated with the steel-pickling operation and controlled by the pickling requirements for particular steels. Spent pickle liquor is removed for regeneration continuously from both batch and continuous picklers at higher acid concentrations than would be dumped to waste because no acid is neutralized or discarded. However, the process is not designed to keep a sulfuric acid concentration stronger than 25 percent in any pickling tank. To retain flexibility in the pickling operation, all acid makeup is added to the pickling tanks. Rinse waters are used as water makeup for the pickling tanks. To further minimize waste of acid in the rinse waters, improvements of rinsing practices are outlined.

With this process pickling time is decreased because pickling tanks are no longer operated at low acid concentrations. Furthermore, production of steel from batch picklers is increased because a constant high acid concentration is maintained and delays due to dumping, refilling, and reheating pickling tanks are eliminated. Quality control of batch pickling becomes much more efficient because acid and ferrous sulfate concentrations in batch pickling tanks are kept constant.

Through recycling of the free acid and roasting of the ferrous sulfate, the sulfur and the iron in spent pickle liquor are reused. Thus a substantial saving of sulfuric acid is possible.

## INTRODUCTION

When steel is being shaped surface oxidation is unavoidable, because while it is heated for shaping and also during the shaping, oxygen of the air forms  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Fe}_3\text{O}_4$  on the surface. These oxides, identified as scale, must be removed if the steel is to be processed further. Cold-rolled steel sheet and strip would not be uniform and would have objectionable surface imperfections if the scale were not removed before cold rolling. Furthermore, the scale would cause excessive wear on rolls and dies in cold rolling and drawing. Also, metallic coatings would not alloy and adhere satisfactorily, and nonmetallic coatings would not adhere if the oxides were not removed.

Part of the oxide is removed mechanically with high-pressure sprays, scale breakers, and shot blasting. However, pickling, or chemical treatment of the steel surface with an acid-water solution called pickle liquor, must be a final step for satisfactory removal of scale. Sulfuric acid is the most common acid used for pickling. According to information from the National Production Authority, approximately 1 million tons is used annually in the United States. It is low priced, has a negligible vapor pressure in the concentrations used, and among the common acids requires the least storage capacity per ton of 100-percent acid. Hydrochloric, nitric, phosphoric, and hydrofluoric acids also are used for pickling, but their combined tonnage does not equal that for sulfuric acid. This paper presents a process to regenerate spent pickle liquors from picklers using sulfuric acid; therefore, further reference to acid will be to sulfuric acid.

In pickling, the sulfuric acid forms ferrous sulfate with the iron of the steel as well as with the scale. Inhibitors, which are complex organic compounds, are added to the pickling solution to reduce to a minimum the reaction with the iron. Some picklers use wetting agents to reduce the surface tension of the solution and thus permit its easy penetration between cracks in the oxide coating of the steel surface. As pickling continues, the acid concentration decreases, and the ferrous sulfate concentration increases. The pickle liquor becomes spent and is discharged before the ferrous sulfate can precipitate. If the ferrous sulfate did precipitate on the steel surface, the steel would be just as unfit for further processing as when it was coated with oxide.

Steel strip and steel for tin plating are pickled in continuous picklers. A continuous pickler is a series of 4 or 5 covered tanks, each approximately 70 feet long and filled with the pickle liquor. The steel passes through these tanks as a continuous strip at rates up to 600 feet per minute. The time of contact between steel and pickle liquor is about 1 minute. The steel strip is delivered coiled to the picklers; there it is uncoiled, passed through a scale breaker, then through the pickling tanks, finally through rinse tanks, and then recoiled. Continuity is obtained by welding together the ends of the strips, and the continuous strip is cut as coils are re-formed. The pickle liquor is kept at temperatures approaching the boiling point by direct addition of steam. The acid concentrations in the series of tanks are graduated, with the highest concentration in the steel-exit tank. Some installations isolate the liquor in each tank, and part or all of the contents of each tank is dumped as the liquor becomes spent. In modern continuous picklers the pickle liquor cascades from the steel-exit tank progressively through all the tanks until it is discharged continuously from the steel-entry tank. Water, acid makeup, and inhibitors are added continuously to modern continuous picklers.

Carryover from the continuous pickler tanks to the rinse tank constitutes an important loss of pickle liquor. The concentration in the steel-exit tank is kept highest to insure removal of the last traces of scale, and at the high speed the steel travels as much as 15 percent of the acid used, and sometimes more, is carried over to the rinse tanks. The volume of rinse water discharged may be 5 to 15 times that of spent pickle liquor. Dilution of the acid in the rinse water makes recovery of acid or of any byproduct from the rinse water economically impractical. Where neutralization must be carried out to conform to State regulations, the size of the equipment required to neutralize rinse water plus spent pickle liquor is very large.

Batch picklers are used for bars, plates, sheets, pipe, rod, and wire. Batch picklers are open tubs or vats in which a bath of acid solution is kept at lower temperatures than is usual for continuous pickling. The steel being pickled is placed in the bath from 5 minutes to well over 1 hour, depending on the type of steel being pickled, the amount of scale present, and the temperature and acidity of the bath. All except the very large plates are agitated in the bath. Inhibitors, wetting agents, and foaming agents, which keep down vapor rising from the pickle liquor, are added at the discretion of the pickling foreman. The spent pickle liquor from batch pickling is dumped at a higher ferrous sulfate concentration and a lower acid concentration than can be discharged from continuous pickling because the latter is a relatively high-speed operation and the acid concentration in the continuous pickler tanks must be high.

#### SPENT PICKLE LIQUOR AS STREAM POLLUTANT

Spent pickle liquor is the waste from the pickling operation and is generally considered worthless. Batch picklers keep down the concentration of acid in dumped batches to as low as 1-1/2 or 2 percent, but usual practice is governed by maximum steel-production schedules and calls for dumping at about 5 percent acid. Continuous picklers rarely discharge solutions of more than 10 percent acid, by weight. Ferrous sulfate content of spent pickle liquor is near saturation, but there is only a small market for this salt. Therefore, the liquor has been discharged into the local streams because that is the cheapest form of disposal.

However, with public awareness of the stream-pollution problem, this easy discharge has generally been made illegal by State ordinance. The Bureau of Fisheries (1, p. 410)<sup>2/</sup> has reported that test fish were killed in 50 to 70 minutes by water at a pH of 3. Fish are killed by acid wastes because of precipitation and coagulation of the mucus on their gills and by coagulation of the gill membranes themselves. Both the acid and the ferrous sulfate in spent pickle liquor, when dumped into streams, strip those streams of their protective devices by disrupting the balances of nature. Communicable diseases are spread by human contacts with streams that have been thus stripped of their protective devices. Polluting a stream with spent pickle liquor is harmful to industry, and downstream factories are unreasonably burdened with expensive water-treatment plants because of spent pickle liquor discharged upstream.

#### NEUTRALIZATION OF SPENT PICKLE LIQUOR

The commonest practice for abating pollution from spent pickle liquor is neutralization (2). In neutralization the spent pickle liquor is reacted with lime or limestone in large installations that produce a sludge and a solution saturated with calcium sulfate. Some installations discharge the solution to the local streams and lagoon the sludge, others lagoon everything, and still others discharge the saturated solution to the local streams and use the sludge as an additive in manufacturing cement. The discharged solution, saturated

<sup>2/</sup> Underlined numbers in parentheses refer to items in the bibliography at the end of the report.

with calcium sulfate, hardens the waters of the local streams, imposing an added treatment cost to those who must use stream water in a manufacturing process. Lagoons for the sludge are necessarily huge because the sludge loses moisture very slowly.

The operating cost of neutralization is said to be high. The cost to neutralize a ton of acid used for pickling is reported to be now somewhat higher than the original cost of the acid (3), free and combined as ferrous sulfate, which is discharged in spent pickle liquor.

#### OTHER METHODS FOR TREATING SPENT PICKLE LIQUOR

It is reported that some small steel plants are fortunate enough to be able to sell their spent pickle liquor entirely to pigment manufacturers. Other small plants neutralize all the spent pickle liquor with scrap iron to form a ferrous sulfate crystal useful for sewage treatment and pharmaceutical and pigment manufacturing. Zinc, aluminum, copper, and other sulfate salts are also produced with spent pickle liquor (4); however, the market for all these products is small.

A proposal has been made to mix the spent pickle liquor with blast furnace slag in open pits (5). Another proposal has been made to combine the spent pickle liquor with coke-oven gas to form ammonium sulfate (6); however, this method is handicapped because the coke-byproduct plant and the pickling departments are invariably at opposite ends of a steel plant. Proposals have been made to use the spent pickle liquor to leach low-grade manganese ores (7), but the distance between the manganese deposits and steel plants is too great for this to be economical. A regenerative scheme takes advantage of the fact that ferrous sulfate is insoluble in certain aliphatic organic compounds (8); however, inevitable loss of the organic compounds plus the need to remove water that accumulates in the pickling tanks may cause the process to be even more expensive than the neutralization methods.

#### NEED FOR CONSERVATION

The yearly consumption of sulfuric acid in the United States is expected to continue to increase, but the rate of supply of sulfur and pyrite for its manufacture is not expected to increase as rapidly (9). Disrupting shortages of sulfuric acid have occurred in the past and will continue to occur (10). Furthermore, the days of cheap sulfuric acid appear to be at an end, and all users of sulfuric acid must plan to economize. Spent pickle liquor contains not only the unwanted ferrous sulfate but also free sulfuric acid. Analysis of typical spent pickle liquor reveals that 30 to 50 percent of the acid fed to a pickler is discharged as free acid. This discharge is not due to poor operation but to the need to discharge the ferrous sulfate that is in solution along with the free acid.

Coupled with the need to conserve sulfuric acid is the need to conserve the usefulness of the country's streams. The acuteness of this last need has given rise to regulatory statutes in many States. In order to conform to the regulations, the steel industry is spending millions of dollars annually for

new waste-disposal units, as well as for operating expenses of existing units. Some steel plants must treat their waste waters not only to conform to State regulations but to conserve water, which to those plants is a scarce commodity. The Kaiser steel plant at Fontana, Calif., is an example of the great efforts made by industrial plants to conserve water (11).

As has been stated before, the most common practice for abating pollution from pickle liquor is neutralization. When spent pickle liquor is neutralized not only is the free acid lost but also the lime used for neutralization. Neutralization also consumes much energy and manpower in transporting the sludge to lagoons. Furthermore, the huge lagoons required to receive the sludge from neutralization tie up land that could otherwise be used for production units.

Therefore, for the spent-pickle-liquor problem a new approach is necessary that considers the need for conservation of materials, energy, and manpower. Regeneration of the liquor must be carefully studied.

#### REGENERATION PROCESSES THAT DEPEND ON EVAPORATION

The dominant factor that keeps spent pickle liquor in the category of a problem is the fact that each steel plant has to dispose of or treat huge amounts of a very dilute acid solution. Available markets for the byproducts that could be manufactured with spent pickle liquor just are not large enough. The practice of combining the spent pickle liquor with acid rinse waters and other industrial wastes presents additional obstacles to solving the problem. Neutralization is a negative and very expensive solution. The rational solution is to regenerate economically the useful constituents of spent pickle liquor.

The fundamental reason for discarding spent pickle liquor is the need to remove ferrous sulfate, which would otherwise precipitate on the steel. The free acid in spent pickle liquor could be made available for reuse if it were disassociated from the ferrous sulfate and also concentrated to process requirements. Therefore, early workers sought to develop processes that would evaporate some of the water from the spent pickle liquor to precipitate and thus remove ferrous sulfate as crystals.

An early attempt evaporated all the water in a kiln in which concurrently the free acid was completely neutralized by iron oxide dust (12). The ferrous sulfate produced was rekilned to produce sulfur dioxide for a contact sulfuric acid plant. The chemistry of this process is sound, but the attempted commercial-scale application failed owing to extensive corrosion problems. Since then a sintering plant has been proposed to replace the reducing kiln and an atmospheric evaporator to replace the evaporating kiln (13). Despite these changes, the entire process is still practical only for very large capacities and it consequentially requires a very large capital outlay for something that did not succeed in counterpart.

Another process calls for evaporation by spraying spent pickle liquor into a stream of hot combustion gases (14). This process is chemically sound but has not been put into commercial operation because of the large capital outlay required even for a plant of small capacity.

Submerged combustion to evaporate water from spent pickle liquor, and therefore to regenerate the liquor, is practiced in Great Britain (15). Entrainment of droplets of acid solution in the escaping gaseous products of combustion from the submerged combustion heater is unavoidable, therefore special equipment to remove the droplets must be provided. Where the droplets are washed into the sewer an atmospheric-pollution problem can become a stream-pollution problem. If this and related problems can be solved economically, this process may be practical.

Vacuum crystallization is a well-established and dependable method of evaporation. Operated at lower temperatures than atmospheric evaporation, it produces ferrous sulfate septahydrate, which must be dehydrated for most ultimate uses.

The new Blau-Knox-Ruthner process is being given current publicity in steel trade journals (16). After evaporation, ferrous sulfate is reacted with hydrogen chloride gas to produce ferrous chloride and sulfuric acid. The sponsoring company states about this process, "Meanwhile, we want the industry to know about this development without encouraging premature proposals."

Regeneration by atmospheric evaporation is the most promising of all the regenerative schemes; but the acceptable process must be operated in the most economical manner possible, and the process must be carried out in a small, simple installation that does not interfere with the best pickling practices.

#### PROPOSED PROCESS FOR REGENERATING SPENT PICKLE LIQUOR

This proposed process for regenerating spent pickle liquor is integrated into the pickling operation and is controlled by the pickler's requirements for pickling steel. Regeneration is a closed system from which no liquor is discharged and only evaporated water and crystallized ferrous sulfate monohydrate are removed. Process details, including materials and heat balances, are given in the appendix. Figure 1 is an overall flow diagram for regeneration; figure 2 a flow diagram for the regeneration plant; figure 3 a flow diagram for the continuous pickler; and figure 4 a flow diagram for the batch pickler. The size of the regeneration equipment applies to a hypothetical steel plant consuming 87-1/2 tons daily of 66° B. sulfuric acid for all pickling operations when no regeneration is practiced.

Concentration of sulfuric acid in the steel-exit tank of the continuous pickler is kept as in current practice at about 25 percent by weight. By cascading a greater flow of pickle liquor through the other tanks, an acid concentration of approximately 20 percent is kept in the steel-entry tank. This 20-percent acid solution overflows into a 2,000-gallon, lead-lined steel tank, from which it is pumped through lead-lined steel pipe directly to the evaporator.

The acid concentration in the batch pickler is kept constant at about 20 percent acid by weight. The rate of flow of regenerated acid to the batch-pickler tank is adjusted to the quantity and type of steel being pickled. Overflow rate from the batch pickler tank into a 1,000-gallon, lead-lined

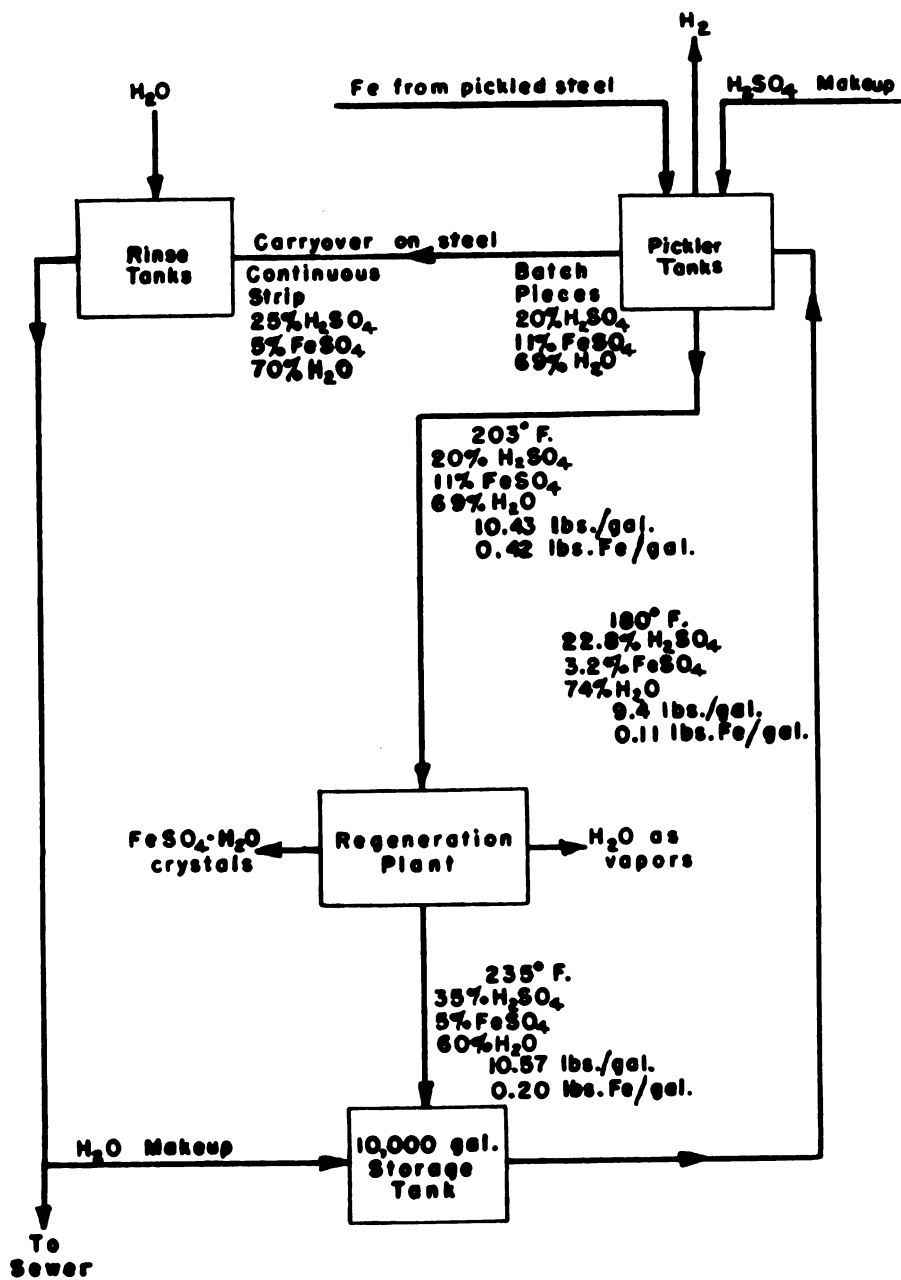


Figure 1. - Overall flow diagram for regeneration.

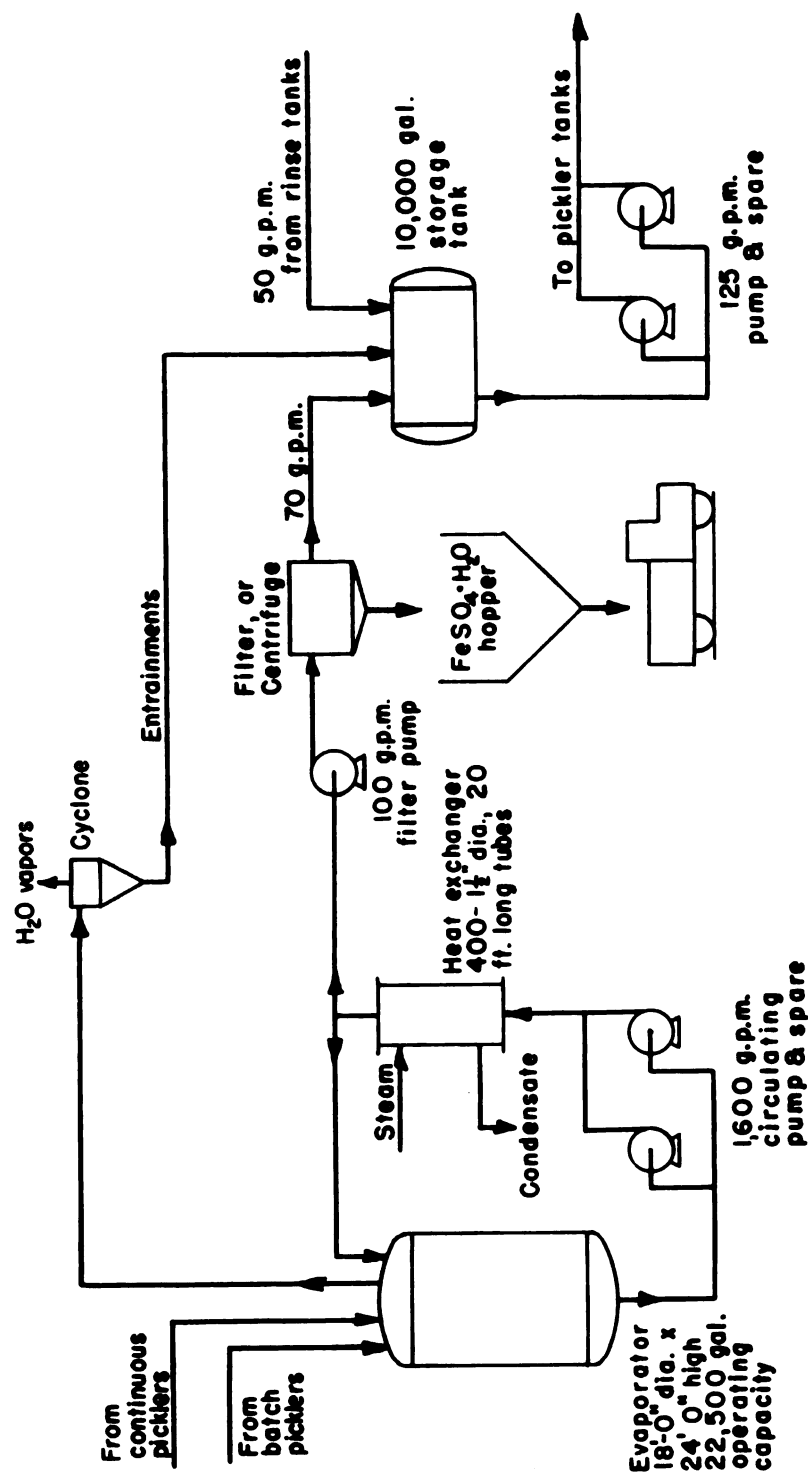


Figure 2. - Regeneration plant.

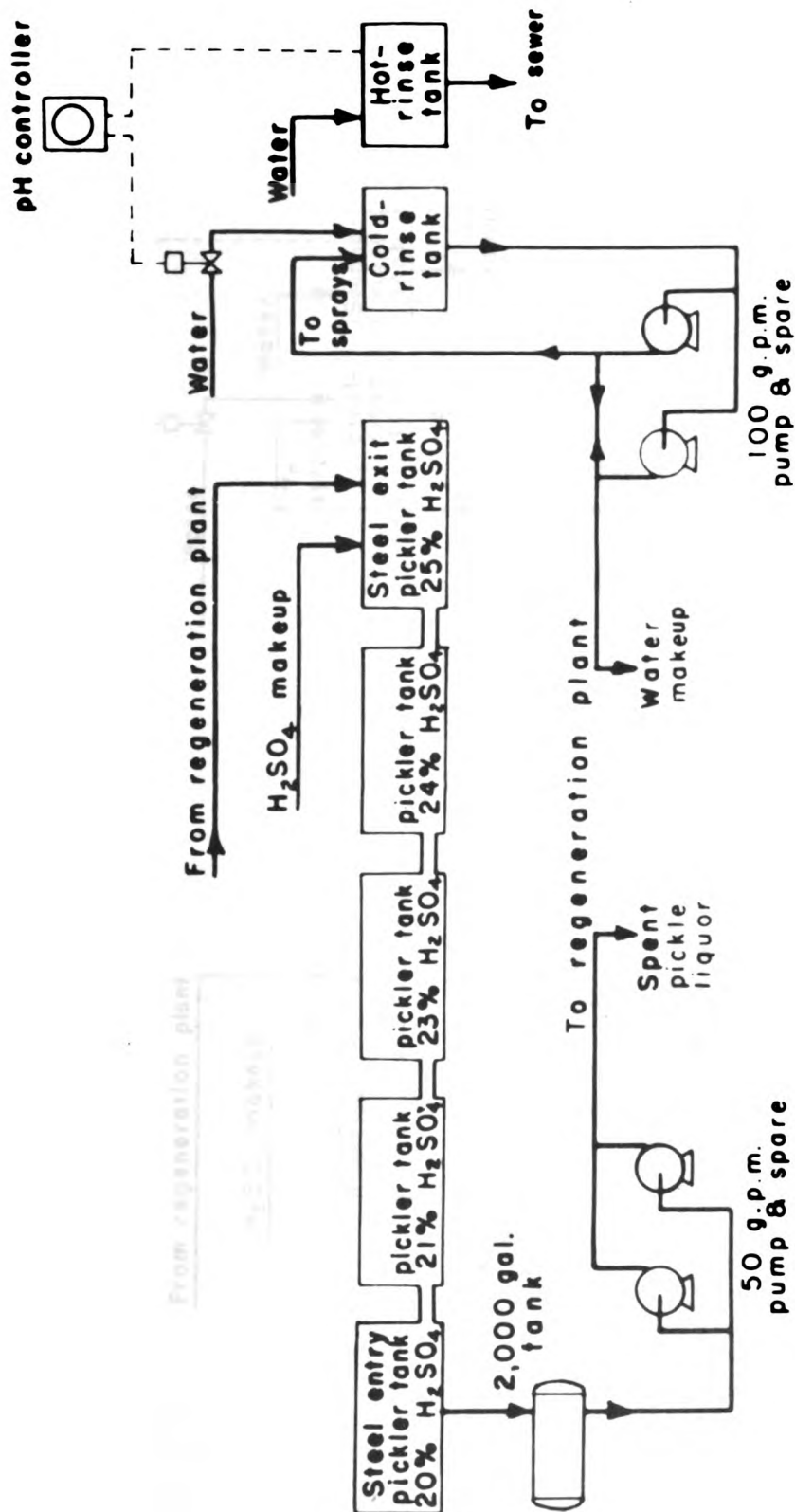


Figure 3. - Continuous pickler.

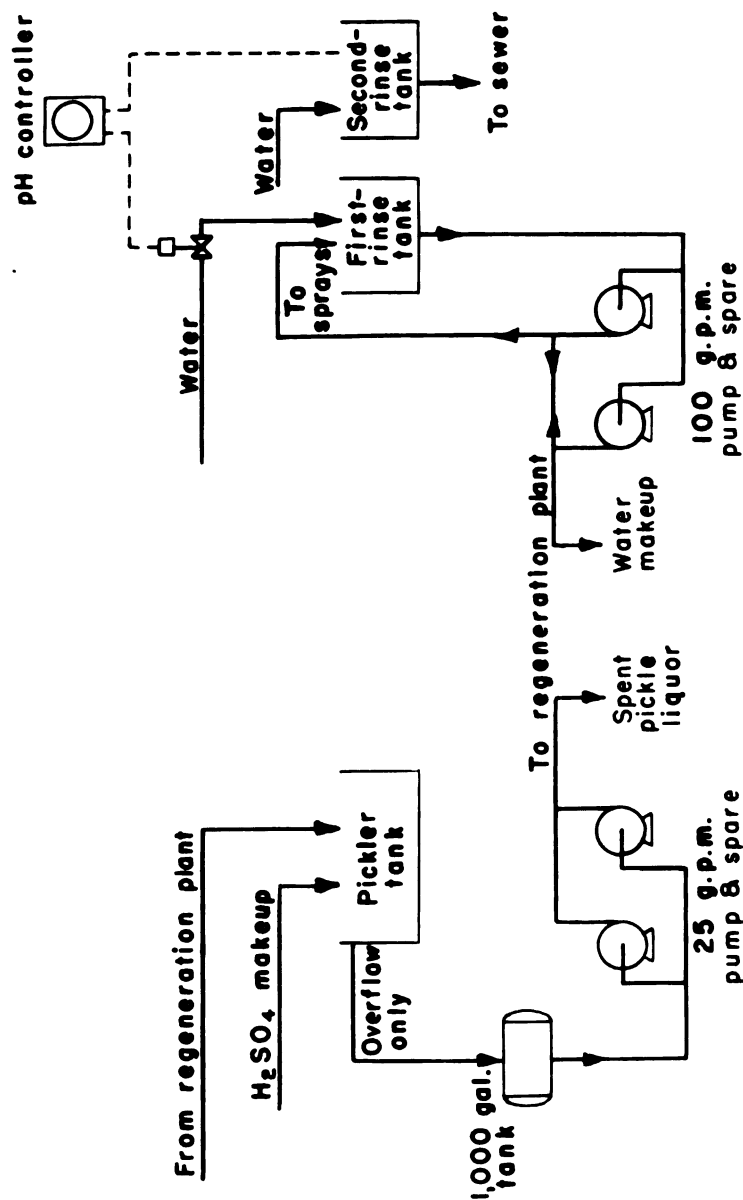


Figure 4. - Batch pickler.

steel tank is a consequence of the flow of regenerated acid. The overflow is pumped to the evaporator through lead-lined steel pipe.

A slurry of ferrous sulfate monohydrate crystals in a 35 percent  $H_2SO_4$ -5 percent  $FeSO_4$  solution boiling at about  $235^{\circ}F$ . is kept in the evaporator. A pump circulates the slurry through the tubes of a one-pass heat exchanger at approximately 10 feet per second. Heat for evaporation is supplied by condensing steam in the shell of the heat exchanger. The evaporator is lined with 1/4-inch lead sheet. The tubes of the heat exchanger are Hastelloy. From the slurry outlet pipe of the heat exchanger, a pipeline goes to the suction of a filter pump, which feeds the continuous pressure filter. The filter parts that are in contact with pickle liquor are either Hastelloy or lead-lined steel. The crystals are filtered hot under pressure because, in the temperature range of crystallization, their solubility increases with temperature drop. The wash water for the filter comes from the rinse tanks. The crystals from the filter are dumped to a wooden hopper from which they are dumped either to a truck or a gondola railroad car. The filtrate flows by gravity to a 10,000-gallon, lead-lined steel tank. This filtrate is an acid solution saturated with ferrous sulfate. To prevent precipitation of ferrous sulfate crystals from this solution, the water makeup for the pickler tanks is added to the 10,000-gallon tank. This addition dilutes the regenerated pickle liquor to a solution that contains 22.8 percent sulfuric acid and only 0.11 lb. of Fe per gallon (see fig. 1). Therefore, ferrous sulfate crystals cannot precipitate in the 10,000-gallon tank or in the pipelines to the pickler tanks. This water makeup is pumped from the rinse tanks, as described below, and delineated on figures 3 and 4. The vapors from the evaporator pass through an insulated, lead-lined cyclone, and any entrained solution removed flows by gravity to the 10,000-gallon tank. All pumps except the filter pump are paired with a spare.

To reclaim the maximum amount of acid carried over into the cold-rinse tank, improvements are recommended in rinsing (see fig. 3). The cold-rinse tank of the continuous pickler is equipped with a roll that will hold the strip above the liquid contents for a short space. The cold rinse water is recirculated through high-pressure sprays, which wash away carried-over acid solution from both faces of the strip being held above the liquid contents. Cold-water makeup is added direct to the tank, and a wetting agent is added to facilitate washing. From the discharge of the spray pump a pipeline sends part of the recirculated cold rinse water as makeup to the 10,000-gallon tank (see fig. 2).

A maximum of carryover acid is reclaimed similarly in the first rinse tank of the batch pickler (see fig. 4). This first rinse tank is also equipped with high-pressure sprays and a circulating pump. Makeup to the 10,000-gallon tank is taken from the discharge of this circulating pump. The steel is rinsed again in the second rinse tank for control.

It is proposed to locate mechanical devices, such as squeegee rolls, between the cold-rinse tank and the hot-rinse tank similar to those between the pickling tank and the cold-rinse tank of the continuous pickler. Therefore, carryover of acidic cold rinse water into the hot-rinse tank is kept to a minimum. In the batch pickler enough time is taken to permit maximum drainage

before the steel is placed in the second-rinse tank. The volume of water flow to the hot-rinse tank of the continuous pickler and the second-rinse tank of the batch pickler is at constant, economically maximum rates. The pH controller at the continuous pickler (see fig. 3) will cause an increase of water makeup to the cold-rinse tank if the pH falls low enough to prevent satisfactory rinsing. Likewise at the second-rinse tank of the batch pickler the pH controller (see fig. 4) will cause an increase of water makeup to the first-rinse tank if the pH falls. The sample of the hot rinse water activating the pH controller may be cooled for maximum efficiency.

It is to be noted that, in this proposed method of regenerating spent pickle liquor, steel rinsing becomes a two-step operation. The first rinsing step will use an amount of water, which will be approximately that needed for makeup to the pickler tank. Therefore a maximum amount of acid carried over on the steel surface will be reclaimed. Keeping the pH of the water from the second rinsing step high enough will complete the rinsing of the steel and obviate the need to treat any discharged rinse water. The pH control is primarily to protect the steel by assuring complete rinsing.

From the 10,000-gallon tank a pump continuously sends the regenerated solution, diluted with the water makeup from the rinse tanks, back to the pickler tanks (see fig. 2). Sulfuric acid makeup and pickling inhibitors are added to the pickler tanks. The concentration of iron in the aggregate feed to each pickler tank is kept down to only 1/10 pound of iron per gallon of feed solution.

#### INCREASED PICKLING CAPACITY; BETTER QUALITY CONTROL

In current continuous pickling practice the tank from which spent pickle liquor is discharged is so low in acid concentration that pickling is very slight in that tank. The proposed process of regeneration calls for keeping a high acid concentration in that tank. Therefore, with one more effective pickling tank in the line, speed of strip travel is increased through all the tanks, and production of pickled steel is consequentially increased.

Under the proposed process of regeneration, in the batch pickler the steel is constantly exposed to a high acid concentration. Therefore, a very significant improvement will be made over current pickling practice in which the steel is being pickled for long periods with acid concentrations not quite low enough for dumping. Furthermore, with regeneration no time is lost in dumping batches, refilling, and reheating the contents of the pickler tank. At the beginning of a week, the batch left over from the previous week is ready. The continuous feed of regenerated solution is started, it overflows to the regeneration plant, and pickling proceeds with no delays until the end of the week. Accumulations of dirt or other undissolved matter may be continuously removed through a scavenging system, such as twin filters installed in the pipeline to the regeneration plant.

Steel production obviously will increase with this process of regenerating spent pickle liquor. It would require pilot-plant studies made at a particular steel plant to reveal what the increase shall be for that steel plant.

In current practice of batch pickling, quality control of the product is made difficult because of the constantly changing acid and ferrous sulfate concentrations. However, with constant concentrations made possible by pickle liquor regeneration, better quality control will be achieved.

#### SUGGESTED USES FOR FERROUS SULFATE MONOHYDRATE REMOVED

The ferrous sulfate monohydrate removed in the regeneration plant should not be discarded. Just how it should be used would be influenced by the amount available from a particular steel plant or from a steelmaking area with several plants. When the ferrous sulfate monohydrate available is equivalent to 200 tons or more daily of 66° B., sulfuric acid, it could be roasted to produce a sulfur dioxide gas, which would be suitable for an economically attractive contact sulfuric acid plant.

The Dorr Co. of Stamford, Conn., reports:

Dry ferrous sulfate hydrate crystals may be used in a standard Dorr Co. pyrite roaster as a coolant instead of spray water to absorb the exothermic heat of the pyrite oxidation.

The decomposition of the hydrate crystals produces  $\text{SO}_2$ , which increases the normal strength of the stack gases going to the sulfuric acid plant. Balanced roaster operation at 900° C. requires 0.8-1.0 tons of dry mono- and dihydrate crystals per ton of pyrite feed, and the stack gases contain 18 to 22 percent  $\text{SO}_2$  on a dry basis. About 1.6 tons of mixed feed are required to produce 1 ton of  $\text{SO}_2$ . Typical iron oxide calcines produced contain less than 0.3 percent total sulfur (1.0 percent sulfide sulfur).

Ferrous sulfate hydrate crystals may also serve in a Fluosolids roaster as the only source of  $\text{SO}_2$  for acid production. In this case decomposition is carried out at about 900° C. in a single-chambered reactor, and the heat of decomposition is provided by the combustion of a fuel directly in the fluidized bed of calcine. The decomposition of dry  $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$  requires 85 gallons of Bunker C oil per ton of  $\text{SO}_2$  produced, and the stack gas analyzes approximately 10.5 percent  $\text{SO}_2$ , 16 percent  $\text{CO}_2$ , and remainder  $\text{N}_2$  (dry bases), with small amounts of  $\text{O}_2$ . For the production of  $\text{SO}_2$  gas strong enough for commercial acid production, the hydrate crystals fed to the reactor must contain only 1-3 waters of hydration. Copperas ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) must be pretreated to make an acceptable reactor feed.

Predictions for the performance of Fluosolids roaster on ferrous sulfate hydrates and on mixtures of the hydrates and pyrite are based on the results of small-scale pilot-plant tests and on the performance results of large-scale standard pyrite roasters.

The Fluosolids roaster treats its charge with the well-known fluidization technique. By using fluidization, formation of  $\text{SO}_3$  experienced in older types of roasters is kept to a minimum. Of particular interest to integrated steel

mills is that hydrogen sulfide gas may be used both as a fuel and as a source of sulfur, when added with air and the ferrous sulfate alone to a fluidization roaster. The hydrogen sulfur would be that removed from coke-oven gas, which is thus purified for use in the open hearth.

For steel plants that do not produce enough ferrous sulfate monohydrate for a conventional sulfuric acid contact plant, the new auto-oxidation process may be economical. This auto-oxidation process, first proposed by the Bureau of Mines in 1927 (17) and improved by other contributors (18, 19), calls for roasting ferrous sulfate monohydrate to produce a sulfur dioxide gas. This sulfur dioxide is then bubbled along with air through a very dilute manganous sulfate solution to produce a liquor as high as 60 percent sulfuric acid by weight. The manganous sulfate is the catalyst for the process, and ozone is added to increase the acid concentration that may be produced efficiently. The above-discussed Fluosolids roaster may likewise be used to produce the sulfur dioxide feed for auto-oxidation.

A complete sulfuric acid regeneration and recovery plant would utilize the ferrous sulfate monohydrate for its sulfur content in manufacturing sulfuric acid either in the conventional contact plant or in the auto-oxidation process.

For still smaller amounts of ferrous sulfate monohydrate produced, there are other uses. Ferrous sulfate is used in pharmaceutical manufacturing, in fertilizer manufacture, as a weed killer, as a deodorizer, as a disinfectant, as a decolorizer in the textile industry, for treating plating wastes, as a reagent in analytical chemistry, and for other uses. Ferrous sulfate oxidized to the ferric state is used in water purification and in sewage treatment as a coagulant. The iron content of ferrous sulfate is utilized, after the sulfate is removed, in manufacturing pigments and cosmetics and in illuminating gas purification.

#### DISCUSSION OF ENGINEERING FACTORS FOR REGENERATION

This proposed process for regenerating spent pickle liquor is based largely on the negative solubility slope of ferrous sulfate in the temperature range 160° to 240° F. Selection of specific concentrations have been influenced by the work of Pearson and Bullough (20) of the British Iron and Steel Research Association. However, engineering design of the regeneration process conforms to current American pickling practice. A pilot-plant study of the process is recommended to affirm the engineering factors. The pilot plant must be operated in conjunction with production pickling of steel because the factors of increased production and better quality control are intrinsic to the worth of the process.

## APPENDIX A - PROCESS DESIGN

### Basic Factors From Current Pickling Practice

A steel mill with a pickled-steel production of 5,000 tons per day is used as a basis. Its sulfuric acid consumption, before regenerating the pickle liquor is taken to be 35 pounds 66° B. sulfuric acid per ton of steel pickled. The concentration of the spent pickle liquor from this steel plant, before regeneration, is taken to be  $H_2SO_4$ , 5 percent,  $FeSO_4$ , 18, and  $H_2O$ , 77. To calculate other basic factors, the following assumptions are made, which apply both before and after regeneration:

1. 15 percent of the acid charged to a pickler is lost to rinse tanks, fume scrubbers, and uncontrolled overflow. The largest portion, 13.5 percent, is lost to the cold-rinse tank.
2. The same amount of iron per ton of steel pickled would be removed as ferrous sulfate from the pickler tank, whether or not spent pickle liquor is regenerated.
3. Composition of the pickle liquor carried over by the continuous steel strip into the cold-rinse tank is, in percent: 25  $H_2SO_4$ , 5  $FeSO_4$ , and 70  $H_2O$ ; 5 percent  $FeSO_4$  is equivalent to 3.23 percent  $H_2SO_4$ .

Therefore, for the basic steel plant consumption is:

$$\frac{(5,000 \text{ tons steel})}{\text{day}} \left( 35 \frac{\text{lb. 66° B. acid}}{\text{tons steel}} \right) = 87.5 \frac{\text{tons 66° B. sulfuric acid}}{\text{day}}$$

$$\frac{2,000 \text{ lb.}}{\text{tons}}$$

Using assumption 1,

87.5 (15 percent) = 13.125 tons 66° B. sulfuric acid per day is lost to rinse tanks, fume scrubbers, and uncontrolled overflow. 87.5 - 13.125 or 74.375 tons 66° B. sulfuric acid per day is lost in spent pickle liquor.

Since 66° B. sulfuric acid is 93.19 percent  $H_2SO_4$  by weight,

13.125 (0.9319) 0.9 = 11.01 tons  $H_2SO_4$  (100 percent) is lost per day to rinse tanks.

13.125 (0.9319) 0.1 = 1.22 tons  $H_2SO_4$  (100 percent) is lost per day otherwise.

Using assumption 3,

$\left( \frac{3.23}{25 + 3.23} \right) 100 = 11.44$  percent of the total equivalent  $H_2SO_4$  carried over by the steel strip into the rinse tank is that equivalent in  $FeSO_4$ .

Since 11.01 tons  $\text{H}_2\text{SO}_4$  (100 percent) is calculated to be lost daily to rinse tanks,  $11.01 (0.1144) = 1.26$  tons equivalent  $\text{H}_2\text{SO}_4$  (100 percent) is lost per day in  $\text{FeSO}_4$  carried over into the rinse tanks.

$11.01 - 1.26 = 9.75$  tons free  $\text{H}_2\text{SO}_4$  (100 percent) is carried daily over into the rinse tanks.

$11.01 (0.1144) \left( \frac{55.85 = \text{M.W. of Fe}}{98.08 = \text{M.W. of } \text{H}_2\text{SO}_4} \right) = 0.72$  tons Fe per day in the form of  $\text{FeSO}_4$  is carried over into the rinse tanks.

Further using assumption 3,

$\frac{70}{(25 + 3.23)} (11.01) = 27.30$  tons  $\text{H}_2\text{O}$  per day is carried over into the cold-rinse tank.

Spent pickle liquor with concentration of, 5 percent  $\text{H}_2\text{SO}_4$ , 18  $\text{FeSO}_4$ , and 77  $\text{H}_2\text{O}$  has a density of 10.17 lb./gal. (21, p. 629) and contains 0.67 lb. Fe/gal. Eighteen percent  $\text{FeSO}_4$  is equivalent to 11.62 percent  $\text{H}_2\text{SO}_4$ ; therefore,

100 percent  $\left( \frac{5}{5 + 11.62} \right) = 30.08$  percent of equivalent  $\text{H}_2\text{SO}_4$  discharged in this spent pickle liquor is free  $\text{H}_2\text{SO}_4$ , and 100 percent - 30.08 percent, or 69.92 percent, is equivalent  $\text{H}_2\text{SO}_4$  in  $\text{FeSO}_4$ .

Therefore, volume rate of spent pickle liquor discharged by the basic steel plant before regeneration is in effect is:

$$\frac{(74.375 \frac{\text{tons } 66^\circ \text{ B. acid}}{\text{day}}) \left( \frac{0.9319 \text{ lb. } \text{H}_2\text{SO}_4}{\text{lb. } 66^\circ \text{ B. acid}} \right) \left( \frac{2,000 \text{ lb.}}{\text{tons}} \right)}{\left( \frac{(5 + 11.62) = \text{lb. } \text{H}_2\text{SO}_4}{100 \text{ lb. spent pickle liquor}} \right) \left( \frac{1,440 \text{ min.}}{\text{day}} \right) \left( \frac{10.17 \text{ lb.}}{\text{gal.}} \right)} = \frac{57 \text{ gal.}}{\text{min.}}$$

The iron discharged in this spent pickle liquor is:

$$74.375 (0.9319) 0.6992 \left( \frac{55.85 = \text{M.W. of Fe}}{98.08 = \text{M.W. of } \text{H}_2\text{SO}_4} \right) = \frac{27.60 \text{ tons}}{\text{day}}$$

Therefore:

$27.60 \left( \frac{169.9 = \text{M.W. of } \text{FeSO}_4 \cdot \text{H}_2\text{O}}{55.85 = \text{M.W. of Fe}} \right) = \frac{84 \text{ tons } \text{FeSO}_4 \cdot \text{H}_2\text{O}}{\text{day}}$  is produced in the continuously operated regeneration plant.

However, with regeneration in effect, by using 50 percent of the rinse-water-tank discharge as water makeup for the pickling tanks, 50 percent of the  $\text{FeSO}_4$  in the rinse water is salvaged. This 50 percent is a conservatively low figure used for calculations, although the design of the plant calls for salvaging most if not all of the cold-rinse water. Therefore because 0.72 tons Fe per day are carried over into the rinse tanks, total production of  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  in the regeneration plant is:

$$84 + \frac{0.72}{2} \left( \frac{169.9 = \text{M.W. of FeSO}_4 \cdot \text{H}_2\text{O}}{55.85 = \text{M.W. of Fe}} \right) = \frac{85 \text{ tons.}}{\text{day}}$$

This 85 tons  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  is equivalent to 49.07 tons  $\text{H}_2\text{SO}_4$  (100 percent) and contains 9 tons  $\text{H}_2\text{O}$ . It should be noted that using these basic factors, the steel's weight loss owing to pickling is calculated to be:

$$100 \left( \frac{27.60 + 0.72}{5,000} \right) = 0.57 \text{ percent.}$$

#### Weights and Volumes of Flows for Regeneration

The overall flow diagram and the concentrations of basic flows for the regeneration of spent pickle liquor are specified in figure 1.

To secure the weights and volumes of flows for regeneration, calculations are made based on 100 tons of spent pickle liquor (20 percent  $\text{H}_2\text{SO}_4$ , 11 percent  $\text{FeSO}_4$ ) to be regenerated as 35 percent  $\text{H}_2\text{SO}_4$ , 5 percent  $\text{FeSO}_4$ :

Let  $x$  = weight of  $\text{H}_2\text{O}$  evaporated,

$y$  = weight of  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  produced,

$$(100-x-y) 0.35 = 20 \text{ tons } \text{H}_2\text{SO}_4 \text{ going to the regeneration plant,}$$

$$11 - \left[ y \left( \frac{151.9 = \text{M.W. of FeSO}_4}{169.9 = \text{M.W. of FeSO}_4 \cdot \text{H}_2\text{O}} \right) \right] = \frac{5}{100} (100-x-y) = \text{Tons FeSO}_4,$$

in the solution discharged by the regeneration plant.

It should be noted that  $100-x-y$  includes both the moisture (which is of the same composition as the mother liquor) that is discharged with the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and the mother liquor itself that is discharged by the pressure filter for eventual return to the pickling tanks.

$$\text{Therefore, } 11 - \left[ y \left( \frac{151.9}{169.9} \right) \right] = \frac{5}{100} \left( \frac{20}{0.35} \right) = 2.86,$$

so that  $y = 9.10$  tons  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  produced per 100 tons spent pickle liquor to be regenerated.

$$(100-x-9.10) 0.35 = 20$$

Therefore  $x = 33.76$  tons  $\text{H}_2\text{O}$  evaporated per 100 tons spent pickle liquor to be regenerated.

For a day's operation in which 85 tons  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  is produced

$$85 \left( \frac{100}{9.10} \right) = 934 \text{ tons spent pickle liquor is pumped daily to the regeneration plant.}$$

$$33.76 \left( \frac{934}{100} \right) = 315 \text{ tons } \text{H}_2\text{O} \text{ is evaporated daily at the regeneration plant.}$$

It is now assumed that the 85 tons  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  has 4 tons of mother liquor, or regenerated solution, associated with it. Therefore the daily loss with the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  cake is:

$$\frac{35}{100} (4) = 1.4 \text{ tons } \text{H}_2\text{SO}_4,$$

$$\frac{5}{100} (4) = 0.2 \text{ ton } \text{FeSO}_4, \text{ equivalent to } 0.13 \text{ ton } \text{H}_2\text{SO}_4,$$

$$\frac{60}{100} (4) = 2.4 \text{ tons } \text{H}_2\text{O}.$$

The overall material balance of regeneration is:

|                                                                                  | <u>Tons/day</u>       |
|----------------------------------------------------------------------------------|-----------------------|
| Spent pickle liquor to regeneration =                                            | 934                   |
| $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ removed =                               | 85                    |
| Regenerated solution removed with the $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ = | 4                     |
| $\text{H}_2\text{O}$ evaporated =                                                | <u>315</u> <u>404</u> |
| Regenerated solution returned to pickling tanks =                                | 530                   |

Volume rate of regenerated solution returned to pickling tanks =

$$\frac{530 \frac{\text{tons}}{\text{day}} (2,000 \frac{\text{lb.}}{\text{tons}})}{1,440 \frac{\text{min.}}{\text{day}} (10.57 \frac{\text{lb.}}{\text{gal.}})} = 70 \frac{\text{gal.}}{\text{min.}} \text{ (21, p. 629)}$$

Volume rate of spent pickle liquor to regeneration plant =

$$\frac{934 \frac{\text{tons}}{\text{day}} (2,000 \frac{\text{lb.}}{\text{tons}})}{1,440 \frac{\text{min.}}{\text{day}} (10.43 \frac{\text{lb.}}{\text{gal.}})} = 124 \frac{\text{gal.}}{\text{min.}} \text{ (21, p. 629)}$$

#### Sulfuric Acid Makeup for Regeneration

Enough 66° B. sulfuric acid must be added to the pickling tanks to make up for miscellaneous losses and for the equivalent acid in the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  produced.

|                                                                                                                                                            | <u>Tons of<br/>free H<sub>2</sub>SO<sub>4</sub><br/>(100 percent)<br/>per day</u> | <u>Tons of<br/>equivalent<br/>H<sub>2</sub>SO<sub>4</sub> per day</u> |
|------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| FeSO <sub>4</sub> .H <sub>2</sub> O produced (see p. 13)                                                                                                   |                                                                                   | 49.07                                                                 |
| FeSO <sub>4</sub> removed with the FeSO <sub>4</sub> .H <sub>2</sub> O (see p. 14)                                                                         |                                                                                   | 0.13                                                                  |
| H <sub>2</sub> SO <sub>4</sub> removed with the FeSO <sub>4</sub> .H <sub>2</sub> O (see p. 14)                                                            | 1.40                                                                              |                                                                       |
| FeSO <sub>4</sub> discharged by second rinse tank of batch<br>pickler and hot water tank of continuous<br>pickler<br>1/2 (1.26) (see p. 12)                |                                                                                   | 0.63                                                                  |
| H <sub>2</sub> SO <sub>4</sub> discharged by second rinse tank of batch<br>pickler and hot water tank of continuous<br>pickler<br>1/2 (9.75) (see p. 12) = | 4.88                                                                              |                                                                       |
| H <sub>2</sub> SO <sub>4</sub> Miscellaneous losses (see p. 11)                                                                                            | <u>1.22</u><br>7.50                                                               | <u>49.83</u>                                                          |

$$\frac{(7.50 + 49.83) \frac{\text{ton H}_2\text{SO}_4}{\text{day}}}{0.9319 \frac{\text{ton H}_2\text{SO}_4}{\text{ton 66}^\circ \text{B. sulfuric acid}}} = 61.5 \frac{\text{ton 66}^\circ \text{B. sulfuric acid}}{\text{day}}$$

makeup must be added.

It should be noted that:

$$100 \frac{(87.5 - 61.5)}{87.5} = 29.7 \text{ percent saving in H}_2\text{SO}_4 \text{ consumption is}$$

effected when recycling only is practiced. Further processing the FeSO<sub>4</sub>.H<sub>2</sub>O would salvage the greater part of the rest of the sulfuric acid lost in spent pickle liquor.

#### Water Makeup for Regeneration

|                                                                                           | <u>Tons per day</u>      |
|-------------------------------------------------------------------------------------------|--------------------------|
| Evaporated water (see p. 13)                                                              | 315.0                    |
| Removed in FeSO <sub>4</sub> .H <sub>2</sub> O produced (see p. 13)                       | 9.0                      |
| Removed with FeSO <sub>4</sub> .H <sub>2</sub> O produced (see p. 14)                     | 2.4                      |
| H <sub>2</sub> O carried over to cold-rinse tank (see p. 12)                              | <u>27.3</u><br>353.7     |
| Condensed steam in pickling tanks (assumed and made to allow<br>for miscellaneous losses) | 50                       |
| Water in 66° B. acid makeup (see p. 15)<br>61.5 (1.00 - 0.9319)                           | 4.2 <u>54.2</u><br>299.5 |
| Makeup pumped from cold-rinse tanks to the pickler tank                                   |                          |

## Composition of Aggregate Feed to Pickling Tanks

|                                                   | Tons per day |                  |                                |                   |
|---------------------------------------------------|--------------|------------------|--------------------------------|-------------------|
|                                                   | Total        | H <sub>2</sub> O | H <sub>2</sub> SO <sub>4</sub> | FeSO <sub>4</sub> |
| Regenerated solution (see p. 14)                  | 530          | 318              | 186                            | 26                |
| Condensed steam (assumed)                         | 50           | 50               | -                              | -                 |
| H <sub>2</sub> SO <sub>4</sub> makeup (see p. 15) | 61.5         | 4.2              | 57.3                           | -                 |
| Water makeup from rinse tanks (see pp. 14 and 15) | 305.01       | 299.5            | 4.88                           | 0.63              |
|                                                   | 946.51       | 671.7            | 248.18                         | 26.63             |
|                                                   | 100%         | 70.97%           | 26.22%                         | 2.81%             |

This feed has a density of 9.8 lb. per gal. and contains 0.10 lb. Fe per gal. (21, p. 629).

### Heat Transfer at Regeneration Plant

934 tons daily of spent pickle liquor at 203° F. and 20 percent H<sub>2</sub>SO<sub>4</sub> is concentrated to 530 tons regenerated solution at 235° F. and 35 percent H<sub>2</sub>SO<sub>4</sub> by evaporating 315 tons H<sub>2</sub>O indirectly with steam and then removing 89 tons FeSO<sub>4</sub>·H<sub>2</sub>O gross. The steam source is 140 p.s.i.g. saturated. The temperature of the cooled condensate leaving the heat exchanger and entering the steam trap is 250° F. Therefore, the log mean temperature difference is 60.8° F. The distribution of the heat supplied is:

Heat of vaporization:

$$315 \text{ tons} \left( 2,000 \frac{\text{lb.}}{\text{tons}} \right) 950 \frac{\text{B.t.u.}}{\text{lb.}} =$$

$$\text{B.t.u. per day} \\ 598.5 \times 10^6$$

Sensible heat:

$$934 \text{ tons} \left( 2,000 \frac{\text{lb.}}{\text{tons}} \right) \frac{0.8 \text{ B.t.u.}}{\text{lb.} \cdot ^\circ\text{F.}} (235^\circ\text{F.} - 203^\circ\text{F.}) =$$

$$47.8 \times 10^6$$

Heat of crystallization (the negative of the heat of solution):

$$\frac{85 \text{ tons}}{169.9 \text{ M.W. FeSO}_4} \left( 2,000 \frac{\text{lb.}}{\text{tons}} \right) \left( \frac{1.8 \text{ B.t.u.}}{\text{lb. mol.}} \frac{1 \text{ cal.}}{\text{gm. mol.}} \right)$$

$$\left( \frac{7,350 \text{ cal.}}{\text{gm. mol.}} \right) =$$

$$13.2 \times 10^6$$

Heat of dissociation (the negative of the heat of dilution):

$$20 \text{ percent} (934 \text{ tons}) \frac{2,000 \text{ lb.}}{\text{tons}} (299 - 279) = (21, \text{ p. 310})$$

$$7.5 \times 10^6$$

Heat loss to environment:  
(assumed)

$$\frac{2.2 \times 10^6}{669.2 \times 10^6}$$

or  $27.9 \times 10^6$  B.t.u. per hour is required heat transfer rate.

Assume a constant overall heat transfer coefficient of  $\frac{190 \text{ B.t.u.}}{\text{hr. (sq. ft.)} \cdot ^\circ\text{F.}}$  and constant specific heats. Therefore the required area of heat transfer =

5684

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$$\frac{27.9 \times 10^6 \frac{\text{B.t.u.}}{\text{hr.}}}{\frac{190 \text{ B.t.u.}}{\text{Hr. (sq. ft.)}^{\circ\text{F.}}} (60.8^{\circ\text{F.}})} = 2,415 \text{ sq. ft.}$$

400 tubes, 1-1/2 inch o.d. and 20 feet long, would supply this area with a safety factor.

Assuming 95 percent efficiency of steam consumption, requirements are:

$$\frac{27.9 \times 10^6 \text{ B.t.u./hr.}}{0.95 \left( \frac{1194.6 \frac{\text{B.t.u.}}{\text{lb.}} - 218.5 \frac{\text{B.t.u.}}{\text{lb.}} \right)} = 30,000 \text{ lb./hr.}$$

If the regeneration plant is too far away from the 140 p.s.i.g. steam boilers, the condensate formed by this steam may be utilized in the hot-rinse tank.

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# THE DEVELOPMENT OF PERMISSIBLE REQUIREMENTS FOR SAFE UNDERGROUND DIESEL HAULAGE

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